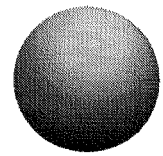

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FINAL REPORT

NATIONAL RENEWABLE ENERGY LABORATORY

DEVELOPMENT OF ASPEN PLUS MODEL OF BIOMASS-TO-ETHANOL PROCESS

TASK ORDERING AGREEMENT NO. KCC-4-13434-00

TASK ORDER NO. 1

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INTRODUCTION

In response to Task Order No. 1 of Task Ordering Agreement No. KCC-4-13434-00, 100% Software Solutions, Inc. has developed a preliminary ASPEN Plus process simulation model of the biomass-to-ethanol process that uses hybrid poplar as a feedstock. This report describes the simulation model, outlines its limitations, and recommends future development work for the model.

OBJECTIVE

A preliminary steady-state process model of the biomass-to-ethanol process which uses hybrid poplar as a feedstock was developed. This model, capable of producing mass and energy balances for the process, will supplement the existing spreadsheet model for the analysis and evaluation of the process. The model uses the ASPEN Plus process simulator. It should enable NREL researchers to more accurately and efficiently evaluate process improvements, with a higher degree of standardization than is possible using the spreadsheet model. In addition, the ASPEN model should be more robust and easier to maintain and enhance than the spreadsheet model.

TECHNICAL BASIS

The ASPEN Plus model was developed based on the technical information contained in the following documents:

- *Appendix A - Statement of Work* of the task order request of proposal
- The NREL draft report *Technical and Economic Analysis of an Enzymatic Hydrolysis Based Ethanol Plant*
- The NREL letter to 100% Software Solutions, Inc. *Questions Concerning the Statement of Work for Task Order No. KCC-4-13434-01*, dated May 20, 1994
- Discussions with NREL personnel on August 23, 1994
- Radian Corporation's *Biomass-to-Ethanol Total Energy Cycle Analysis* report to NREL dated November 21, 1991
- CH2M Hill's *Full Fuel Cycle Analysis of Biomass to Ethanol: Wastewater Treatment System Performance* report to NREL dated December 10, 1991
- Materials provided by NREL personal during the August 23, 1994 meeting, including physical property data, process condition changes relative to those contained in the draft technical report, ASPEN Plus output for modeling cellulose as a polymer, the spreadsheet model source and output, and portions of the Chem Systems reports on their ChemCAD simulation of the biomass-to-ethanol process

MODEL ARCHITECTURE

The process simulation model was developed under Version 9 of Aspen Technologies' ASPEN Plus simulation program.

For ease of use and ease of maintenance, the process model has been divided into ten (10) flowsheet sections: prehydrolysis, liming, solids separation, xylose reaction, cellulase production, SSF reaction, distillation, steam cycle, waste water treatment and boiler. These flowsheet sections correspond roughly to the major process areas as defined in the technical report *Technical and Economic Analysis of an Enzymatic Hydrolysis Based Ethanol Plant.*

Eight process simulation files have been created for the biomass-to-ethanol process model, as outlined in Table 1. The main simulation file (NRELTOT.INP) contains all nine flowsheet sections. The remaining seven simulation files contain stand-alone simulations of the various flowsheet sections. The prehydrolysis, liming, and solids separation sections have been combined into a single simulation file. (Flowsheet diagrams of the models are given with the model descriptions for each section.)

TABLE 1: SIMULATION FILES

INPUT FILE	PROCESS FLOWSHEETS
NRELTOT.INP	All
NRELPREH.INP	Prehydrolysis, liming, solids separation
NRELXYLS.INP	Xylose fermentation
NRELCLSR.INP	Cellulase production and SSF fermentation
NRELDIST.INP	Ethanol Distillation
NRELSSC.INP	Steam Cycle
NRELBOIL.INP	Boiler
NRELWWT.INP	Waste Water Treatment

PHYSICAL PROPERTIES

Because of the time frame for development of this model, the physical property set for simulation is rather crude. Peng-Robinson model is used for all flowsheet sections except the steam cycle, which uses the ASTM steam properties.

COMPONENTS

Table 2 lists the components currently included in the simulation. As indicated in the table, many of the components are non-databank components and have been simulated as other databank components with modified properties.

TABLE 2: SIMULATION COMPONENTS

		DATABANK		NON-DATABANK COMPONENTS	
COMPONENT	ID	YES	NO	MODELED AS	MODIFIED PROPERTIES
water	H2O	X			
cellulose	CELLULOS		X	Dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
xylan	XYLAN		X	Dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
arabinan	ARABINAN		X	Dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
mannan	MANNAN		X	Dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
galactan	GALACTAN		X	Dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
lignin	LIGNIN		X	phenol	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
soluble solids	SOLSLDS		X	Dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
ash	ASH			NC solid	
glucose	GLUCOSE		X	dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
xylose	XYLOSE		X	dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
arabinose	ARABINOS		X	dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
mannose	MANNOSE		X	dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
galactose	GALACTOS		X	dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
cellulase	CELLULAS		X	Dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
biomass	BIOMASS		X	Dextrose	Tc, Pc, Omega, Dgform, Dhform, Plxant, Mw
glycerol	GLYCEROL	X			
acetaldehyde	C2H4O-1	X			
furfural	FURFURAL	X			
HMF	HMF		X	furfural	Mw, Tb
sulfuric acid	H2SO4	X			
calcium hydroxide	CAH2O2	X			
oxygen	O2	X			
nitrogen	N2	X			
carbon dioxide	CO2	X			
ammonia	NH3	X			
methane	CH4	X			
nitrous oxide	NO	X			
nitrogen oxide	NO2	X			
calcium sulfate	CASO4	X			
fusel oil	FUSELOIL		X	iso-amyl alcohol	
gypsum	GYPSUM		X	calcium sulfate	

Note: The following are explanations for the property notations.

- Pc Critical Pressure
- Tc Critical Temperature
- Omega Pitzer's Omega
- Dgform Gibbs free energy of formation
- Dhform Heat of Formation
- Plxant Antoine Ideal Gas Constants
- Mw Molecular weight

Structural formulas and exact molecular weights were specified for all conventional components. Appendix A lists the non-databank physical property data used for the various components. Dextrose was used to model the sugars, but the Aspen databank does not contain Tc, Pc or Antoine Constants for dextrose, so estimated values were used for these values for all components.

MODEL DESCRIPTIONS

PREHYDROLYSIS SECTION

The prehydrolysis simulation contains the prehydrolysis, liming, and solids separations flowsheet sections. It models the biomass-to-ethanol process through centrifugation and subsequent cooling of the liquid streams. Figure 1 shows the prehydrolysis section model.

The prehydrolysis section (flowsheet HYDRL) models the impregnation and prehydrolysis of the feed, and consists of five unit operation models ACIDMIX, ACIDSPLIT, IMRPGNTR, HTR1, and PREHYDRL.

ACIDMIX is a MIXER block and models the addition of the concentrated sulfuric acid feed to the recycle water. The ACIDIN design specification controls the concentration of the dilute acid to 3.0 ± 0.5 wt% acid by manipulating the flowrate of the acid addition. Because the design spec ACIDIN controls the acid concentration at the outlet of the PREHYDRL unit, the ACIDSPLIT unit was inserted to prevent the occurrence of mass balance problems. The stream WASTEACID is the flow of the mixed recycle and water stream which is sent off the flowsheet.

IMPRGNTR models the impregnator and is also an ASPEN MIXER block. Atmospheric pressure is assumed. After the IMPRGNTR, a heater unit HTR1 is added where the addition of Low-pressure steam is used to raise the temperature of stream IMPGFEED to 100°C.

PREHYDRL models the prehydrolysis reactor and is an APSEN RSTOIC reactor block. The reactions are carried out at 160°C and 105 psig. Table 3 gives the reactions modeled and the conversions for those reactions. The flowrate of the high pressure steam feed is manipulated to augment the exothermic nature of the reactions so that the reactor will operate at 160°C. This is done in design spec REACHEAT.

TABLE 3: PREHYDROLYSIS REACTOR STOICHIOMETRIES AND CONVERSIONS

REACTION	STOICHIOMETRY	CONVERSION
Hydrolysis of cellulose, xylose, mannan, and galactan	Cellulose + H_2O → Glucose Mannan + H_2O → Mannose Galactan + H_2O → Galactose Xylan + H_2O → Xylose Arabinan + H_2O → Arabinose	3% of cellulose 80% of Mannan, Xylan Galactan Arabinan
Degradation of cellulose, mannan, and galactan to HMF	Cellulose → HMF + $2H_2O$ Galactan → HMF + $2H_2O$ Mannan → HMF + $2H_2O$	0.1% of cellulose 2.58% of mannan and 2.58% of galactan
Degradation of xylan and arabinan to furfural	Xylan → Furfural + $2H_2O$ Arabinan → Furfural + $2H_2O$	13% of xylan and arabinan

The liming section (flowsheet LIMER) models the blowdown of the prehydrolysis reactor and the overliming reactor. It consists of three unit operation blocks: BLOWDOWN, H2OADDN, and OVERLIME. The unit BLOWDOWN models the prehydrolysis blowdown tank, where the outlet from the prehydrolysis reactor is flashed down to a pressure of 1 atmosphere. An ASPEN FLASH2 block is used to model the flash.

The second block of this section, the H2OADDN block, is needed to properly simulate the water addition at the bottom of the blowdown tank. This water addition must be modeled as a separate step to avoid distorting the flash calculation. If the water stream were added to the flash block, ASPEN would mix it with the other feeds before the flash rather than mixing it with just the flash liquid outlet as desired. The FLSHSLDS design specification is used to control the outlet solids concentration to 12.0 (±0.5) wt% by varying the flowrate of the recycle water addition.

The overliming reactor is modeled as an RSTOIC reactor block. The reaction is specified as adiabatic. Table 4 gives the reactions and conversions used for the reactor. A design specification controls the pH of the reactor outlet to a value of 10.0 (±0.1) by controlling the flowrate of the lime addition stream. See Appendix B for details on the pH calculations.

TABLE 4: OVERLIMING REACTOR STOICHIOMETRIES AND CONVERSIONS

REACTION	STOICHIOMETRY	CONVERSION
Neutralization of Sulfuric Acid with Calcium Hydroxide	$H_2SO_4 + Ca(OH)_2$ → $CaSO_4 \cdot 2H_2O$	100% of sulfuric acid

The solids separation section (flowsheet SOLSEP) models the centrifugation steps between the overliming reactors and the fermentation reactors. Seven unit operation blocks are present: CFUGE1, CFUGE2, FUGLIQMX, BRTHCLR, NEUTRLZR, BTMSLCLR and BTMMIXER.

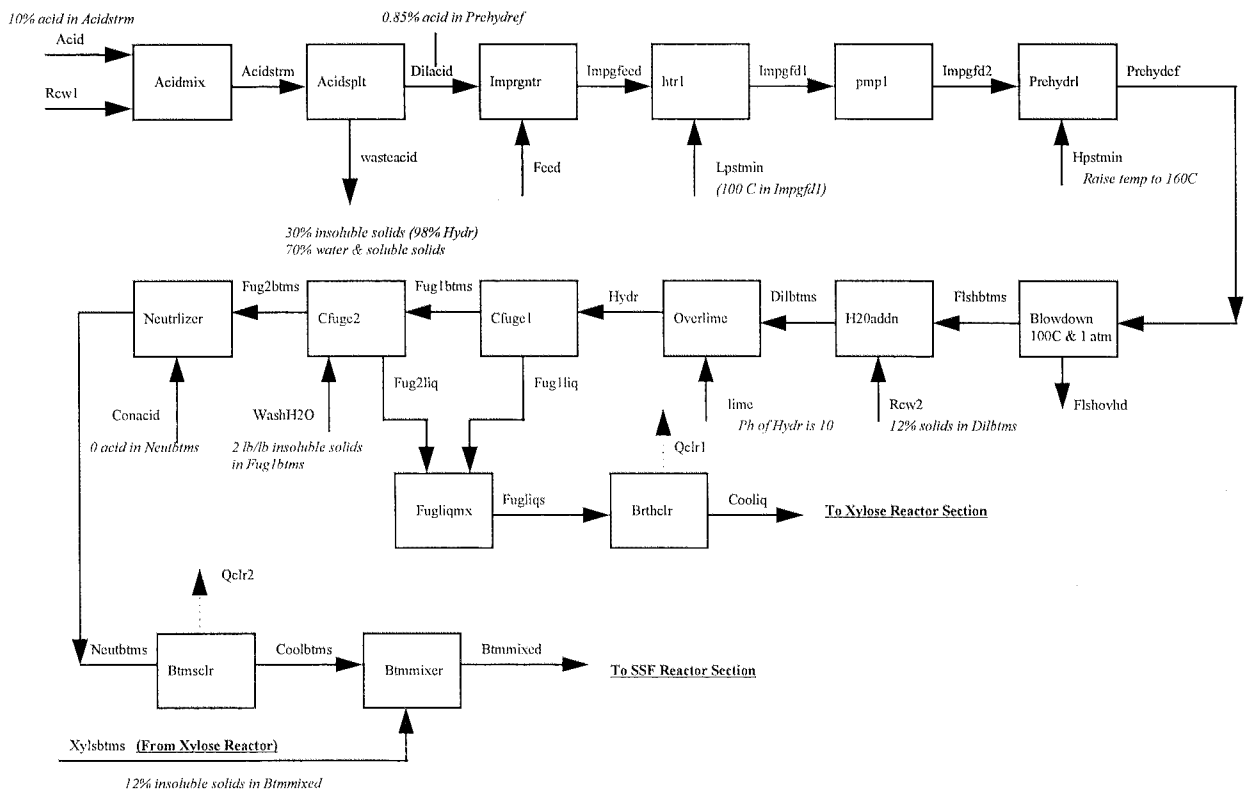
The centrifuges CFUGE1 and CFUGE2 are currently modeled as separators (SEP2). The solid stream flows are split to recover 98% of the insoluble solids in the bottoms stream with the bottoms stream set to contain 30% total insoluble solids.

The FUGLIQMX block is a MIXER UOM used to combine the liquid overflows from the two centrifuges.

The liquid cooler, BRTHCLR, and the bottoms cooler, BTMSCLR, are currently modeled as heater blocks with a temperature specification of 37°C.

The BTMMIXER is a MIXER used to combine the centrifuge bottoms stream after it has been neutralized and cooled (COOLBTMS) and a product stream from the XYLOSE reactor section (XYLSBTMS). The flow of the XYLSBTMS stream is set in a Design-Spec so that the outlet flow of BTMMIXER, stream BTMMIXED, is set to 12% insoluble solids.

Prehydrolysis Section



DESIGN SPECIFICATIONS FOR THE PREHYDROLYSIS SECTION

SLDSSPEC	
Sets	Percentage of solids flow of stream PREFEED to 38.5%
Varies	Mass Flow of stream LPSTEAM
Purpose	Raise the temperature to 100° C

ACIDIN	
Sets	Sulfuric Acid concentration in stream DILACID to 3%
Varies	Mass Flow of stream ACID
Purpose	Sets the acid concentration to be added

ACIDCONC	
Sets	Sulfuric Acid concentration in stream Prehydrl to 0.85%
Varies	SPLIT factor in ACID SPLIT
Purpose	Sets most of acid and recycle water to be added to the system

REACHEAT	
Sets	Heat Duty in stream QPREHYXS to 0
Varies	Mass Flow rate of stream HPSTEAM
Purpose	Maintains the reaction temperature in PREHYDRL

FLSHSLDS	
Sets	Insoluble Solids concentration in DILBTMS to 12%
Varies	Mass Flow of stream RCW2
Purpose	Sets RWC2 flow in flowsheet

PHCONTRL (See Appendix B)	
Sets	pH in stream HYDR to 10.0
Varies	Mass Flow of stream LIME
Purpose	Sets LIME flow

XYLOSE REACTION SECTION

The xylose reaction section models the xylose seed fermentors and the xylose fermentation reactors. Both fermentors were modeled as continuous reactors, using the ASPEN RSTOIC reactor model. Table 5 gives the reaction stoichiometries and conversions for these reactors.

Ammonia was used, in a slight excess (0.2 mole) of demand, as the nitrogen source for biomass cell growth. Reactor temperature was specified as 37°C.

TABLE 5: XYLOSE SEED FERMENTOR STOICHIOMETRIES AND CONVERSIONS

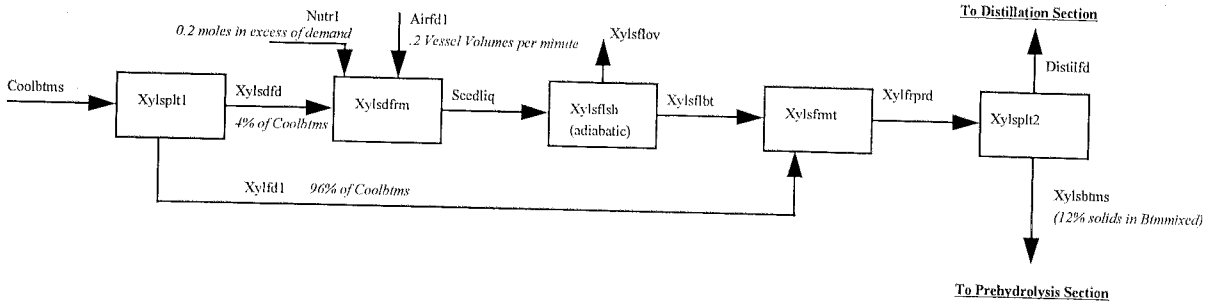
REACTION	STOICHIOMETRY	CONVERSION
Seed Fermentation of glucose, mannose and galactose	3.5 $C_6H_{12}O_6$ + 10.5O_2 + 2NH_3 → Biomass + 15H_2O + 11CO_2	100% Glucose 100% Mannose 100% Galactose
Seed Fermentation of xylose and arabinose	3 Xylose + 4.5O_2 + 2NH_3 → Biomass + 9H_2O + 5CO_2	100% Xylose 100% Arabinose

TABLE 6: XYLOSE FERMENTOR STOICHIOMETRIES AND CONVERSIONS

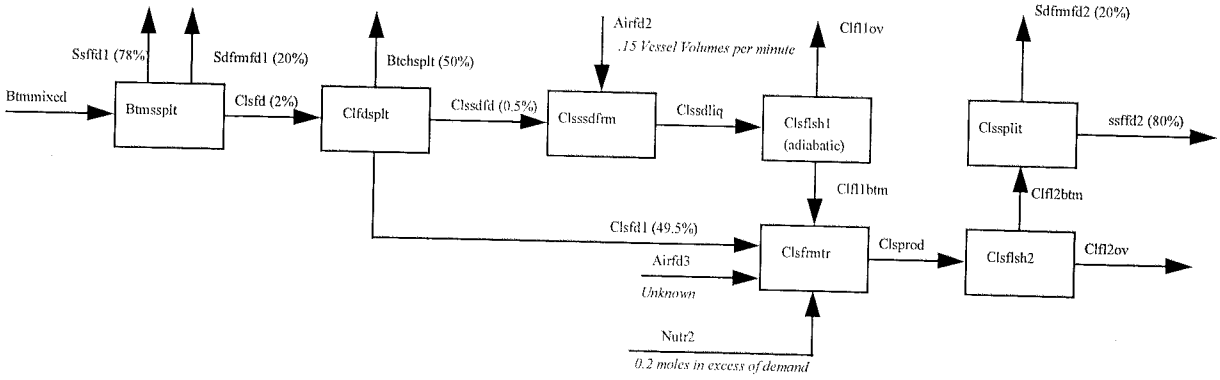
REACTION	STOICHIOMETRY	CONVERSION
Fermentation of glucose, mannose, and galactose	$C_6H_{12}O_6$ → 2 Ethanol + 2CO_2	85.5% Glucose 85.5% Mannose 85.5% Galactose
Fermentation of xylose and arabinose	3 $C_5H_{10}O_5$ → 5 Ethanol + 5CO_2	85.5% Xylose 85.5% Arabinose

An adiabatic flash XYLSFLSH was added after the seed fermentation reactor to remove the gas phase, this flash has a specified pressure drop of 0 psig.

Xylose Reactor Section



Cellulase Reactor Section



The product stream from the Xylose fermentation reactor is sent to a splitter. A portion of the stream XYLSBTMS is sent to the Prehydrolysis section to be mixed with solids stream in unit BTMMIXER. The remainder of the stream is sent to the distillation tower AS-601 as a feed stream.

DESIGN SPECIFICATIONS

SPECAIR1	
Sets	Volume of air to liquid volume in stream
Varies	Mass Flow of stream AIRFD1
Purpose	Provide Flow control on AIRFD1
SPECAIR2	
Sets	Volume of air to liquid volume in stream
Varies	Mass Flow of stream AIRFD1
Purpose	Provide Flow control on AIRFD1

CELLULASE REACTOR SECTION

The feed to the cellulase reaction section, stream Btmmixed, is passed through two splitters BTMSSPLT and CLFDSPLT. The first splitter creates three output streams, SSFFD1 and SDFRMFD1, which are sent to the SSF Reaction Section, and CLSSFD which is sent to the second splitter.

The cellulase reactors model both the cellulase seed fermentor and the cellulase fermentation reactor. Both fermentors were modeled as continuous reactors, using the ASPEN RSTOIC reactor model. Tables 6 and 7 give the reaction stoichiometries and conversions for the individual reactors.

Ammonia was used as the nitrogen source for biomass cell growth. Reactor temperature was specified as 37°C.

TABLE 7: CELLULASE SEED FERMENTER REACTION STOICHIOMETRIES AND CONVERSIONS

REACTION	STOICHIOMETRY	CONVERSION
Seed Fermentation of glucose, mannose and galactose	$3.5C_6H_{12}O_6 + 10.5O_2 + 2NH_3 \rightarrow$ Biomass + $15H_2O + 11CO_2$	100% Glucose 100% Mannose 100% Galactose
Seed Fermentation of xylose and arabinose	$3C_5H_{10}O_5 + 4.5O_2 + 2NH_3 \rightarrow$ Biomass + $9H_2O + 5CO_2$	100% Xylose 100% Arabinose
Fermentation of mannan, cellulose and galactan	$3C_6H_{10}O_5 + 7.5O_2 + 2NH_3 \rightarrow$ Biomass + $9H_2O + 8CO_2$	100% Mannan 100% Cellulose 100% Galactin

TABLE 8: CELLULASE FERMENTER REACTION STOICHIOMETRIES AND CONVERSIONS

REACTION	STOICHIOMETRY	CONVERSION
Glucose, mannose and galactose to Biomass	$3.5C_6H_{12}O_6 + 10.5O_2 + 2NH_3 \rightarrow$ Biomass + $15H_2O + 11CO_2$	47% Glucose 47% Mannose 47% Galactose
Xylose and arabinose to Biomass	$3C_5H_{10}O_5 + 4.5O_2 + 2NH_3 \rightarrow$ Biomass + $9H_2O + 5CO_2$	47% Xylose 47% Arabinose
Mannose, glucose and galactose to Cellulase	$5C_6H_{12}O_6 + 19.75O_2 + 3NH_3 \rightarrow$ Cellulas + $26.5H_2O + 20CO_2$	53% Glucose 53% Mannose 53% Galactose
Xylose and arabinose to Cellulase	$5C_5H_{10}O_5 + 14.75O_2 + 3NH_3 \rightarrow$ Cellulas + $21.5H_2O + 15CO_2$	53% Xylose 53% Arabinose
Cellulose, mannan and galactan to Cellulase	$5C_6H_{10}O_5 + 19.75O_2 + 3NH_3 \rightarrow$ Cellulas + $21.5H_2O + 20CO_2$	100% Cellulose 100% Mannan 100% Galactan

At the outlet of each of the reactors, the product stream is put through an adiabatic flash to remove any vapor products.

The liquid fraction of the flash is sent to a splitter CLSSPLIT which sends two streams SDFRMFD2 and SSFFD2 to the SSF Reaction Section.

SIMULTANEOUS SACCHARIFICATION AND FERMENTATION (SSF) SECTION

The SSF section models the simultaneous saccharification seed fermentor and the simultaneous saccharification fermentation reactor. Both fermentors were modeled as continuous reactors, using the ASPEN RSTOIC reactor model. Tables 8 and 9 give the reaction stoichiometries and conversions for the individual reactors.

TABLE 9: SEED SACCHARIFICATION REACTION STOICHIOMETRIES AND CONVERSIONS

REACTION	STOICHIOMETRY	CONVERSION
Seed Fermentation of glucose, mannose and galactose	$3.5C_6H_{12}O_6 + 10.5O_2 + 2NH_3 \rightarrow$ Biomass + $15H_2O$ + $11CO_2$	100% Glucose 100% Mannose 100% Galactose
Seed Fermentation of xylose and arabinose	$3C_5H_{10}O_5 + 4.5O_2 + 2NH_3 \rightarrow$ Biomass + $9H_2O$ + $8CO_2$	100% Xylose 100% Arabinose
Fermentation of mannan, cellulose and galactan	$3C_6H_{10}O_5 + 7.5O_2 + 3NH_3 \rightarrow$ Biomass + $9H_2O$ + $8CO_2$	14.7% Cellulose 14.7% Mannan 14.7% Galactan

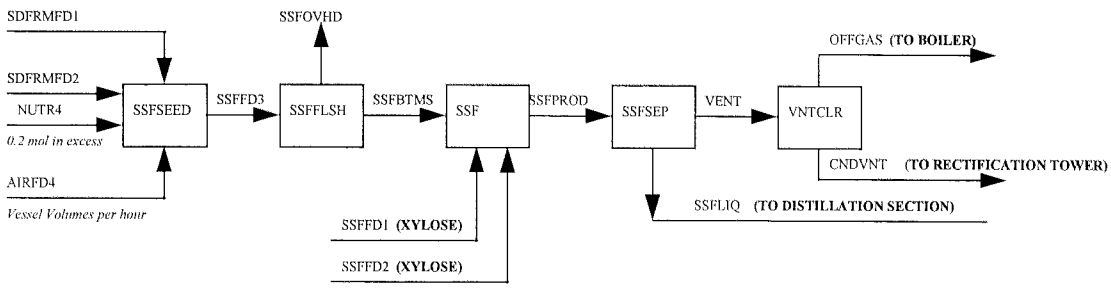
TABLE 10: SACCHARIFICATION FERMENTER REACTION STOICHIOMETRIES AND CONVERSIONS

REACTION	STOICHIOMETRY	CONVERSION
Conversion of cellulose, mannan, galactan to ethanol	$C_6H_{10}O_5 + 1H_2O \rightarrow 2CO_2 + 2C_2H_5OH$	80% Cellulose 80% Mannan 80% Galactan
Conversion of cellulose, mannan and galactan to fuseloil	$C_6H_{10}O_5 + 1H_2O \rightarrow CO_2 + 1.5O_2 + C_5H_{12}O$	0.1% Cellulose 0.1% Mannan 0.1% Galactan
Conversion of cellulose, mannan and galactan to glycerol and acetaldehyde	$C_6H_{12}O_6 \rightarrow CO_2 + C_2H_4O$ + Glycerol	0.5% Cellulose 0.5% Mannam 0.5% Galactan
Conversion of xylan and arabinan to sugars	$C_5H_{10}O_5 + 1H_2O \rightarrow C_5H_{12}O_6$	80% Xylan 80% Arabinan

Between the two fermentation reactors is an adiabatic flash which removes the vapor produced in the Seed Saccharification Reactor. The products from the Saccharification Fermenter are split in a separator, with the vapor fraction sent to a flash VNTCLR and the liquid fraction sent to heat exchanger TT-615 in the Distillation Section.

At the outlet of the flash VNTCLR, the vapor is set to the burner as fuel and the liquid fraction is sent to Tower AS-602 in the Distillation section as one of the feed streams.

SSF REACTOR SECTION



DISTILLATION SECTION

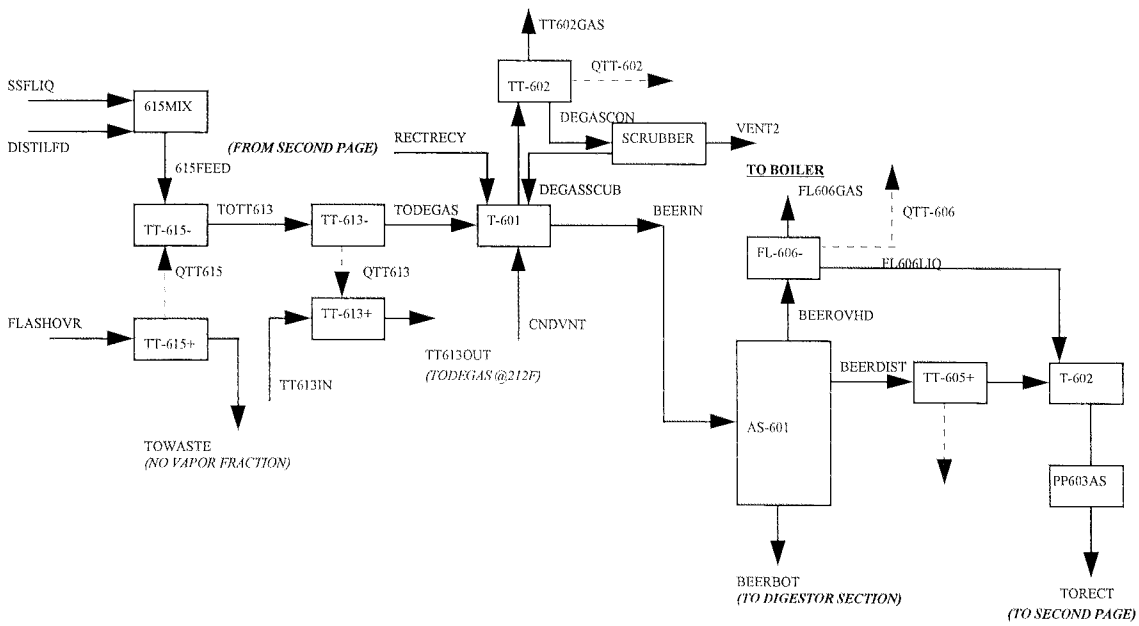
The distillation section models the purification of the ethanol product. This is done in a series of two towers. The first being the Beer Tower and the second being a Rectification Tower. The Beer Tower overhead is sent to the Rectification Tower and the bottoms are sent to the Waste Water Treatment section. The rectification Tower overheads are taken to a molecular sieve purification step, while the bottoms are recycled back to the Beer Tower.

FLOWSHEET COMMENTS. The drawing of this portion of the flowsheet is quite complex, but this is due to the method used to model the heat exchangers. Instead of using the ASPEN Heat Exchanger model. A series of heaters and coolers with intermediate heat streams has been used. This results in a much faster convergence of the flowsheet without any reduction in accuracy. However, it creates two units and an additional stream for each heat exchanger. The nomenclature used in this flowsheet is for the hot side of the exchanger to be labeled as (+) and the cold side be labeled as (-).

PROCESS DESCRIPTION. The liquid stream from the separator SSFSEP is sent to TT-615- where it is heated against the vapor stream Flshovhr from the Prehydrolysis section. The specification on this exchanger is that the stream Flshovhr is completely condensed.

The stream is then further heated to 100°C in TT-613- against low pressure steam. It is then mixed with the Rectification Tower (AS-602) bottoms and the recycle from the vapor condensation and then flashed. The liquid product is then mixed with DISTILFD stream from the XYLSSPLT and fed to the Beer Tower.

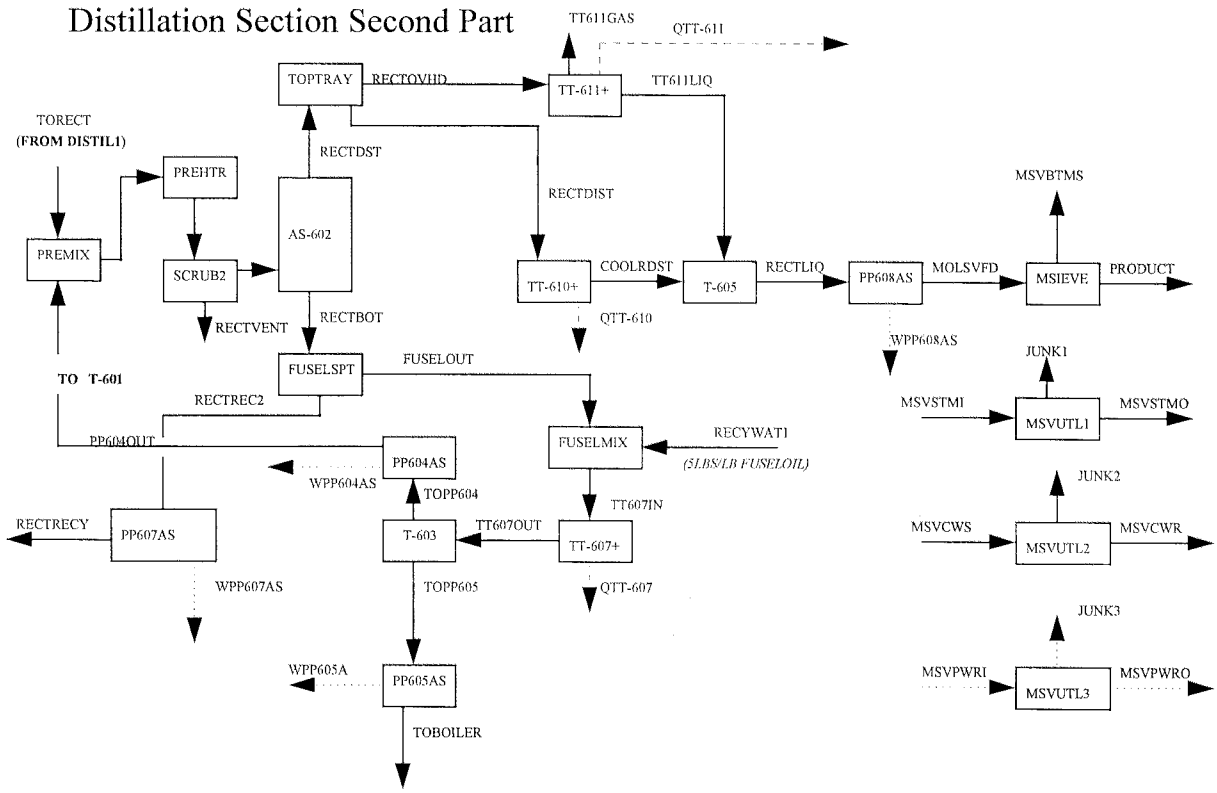
DISTILLATION SECTION FIRST PART



The Beer Tower Overhead (BEEROVHD) is flashed and cooled against cooling water. The Vapor stream is sent to the Boiler Section where it is used as fuel. The liquid stream is mixed with the distillate from the Beer Tower in the mixing tank T-602.

The Beer Tower Distillate is cooled against cooling water to 155°F in TT-605+ and then sent to T-602. The mixing tank product is pumped to 50 psi and then fed into the Rectification Tower.

The Beer Tower bottoms are sent to the Waste Water Treatment Section.



The Rectification Tower has three feed streams. One is the distillate from the Beer Tower. The second is the liquid fraction (CNDVNT) from the SSF Section product flash (VNTCLR). The third is a diluted side draw from the Rectification Tower (PP604out).

The Rectification Tower overhead (RECTOVHD) is flashed and cooled against cooling water to 150°F in TT-611+. The vapor fraction (TT611GAS) is sent to the FUELMIX block in the Boiler Section to be used as fuel. The liquid fraction is sent to a mixer (T-605) where it is mixed with the cooled distillate (171°F) from the Rectification Tower. The product stream from T-605 is pumped to 60 psi and sent to the molecular sieve for further purification.

The sidedraw from the Rectification Tower (fuselout) is sent to a mixer where it is diluted with recycled water. This mixture is cooled in TT-607+ to 100°F and then split in T-603.

The split factors are set so that 100 percent of the ethanol is placed in stream TOPP605, 100% of the Fuseloil and 50% of the water are placed in stream TOPP604.

The stream TOPP605 is sent to a pump to raise its pressure to 60 psi and then the stream is sent to FUELMIX in the Boiler Section to be used as fuel for the Boiler.

The stream TOPP604 is pumped to 50 psi and then input back into the Rectification tower.

DESIGN SPECIFICATIONS

TT602FLO	
Sets	Heat Duty of stream QTT602XS to 0
Varies	Mass-flow of cooling water in stream TT602CWS
Purpose	Sets amount of cooling water needed in HEX TT-602-
TT613FLO	
Sets	Heat Duty of stream QTT613XS to 0
Varies	Mass flow of stream TT613IN
Purpose	Sets amount of steam needed in TT-613+
TT606FLO	
Sets	Heat Duty of stream QTT606XS to 0
Varies	Mass Flow of stream TT606CWS
Purpose	Sets amount of cooling water needed in HEX TT-606-
TT607FLO	
Sets	Heat Duty of stream QTT607XS to 0
Varies	Mass flow of stream TT607CWS
Purpose	Sets amount of cooling water needed in HEX TT-607-
TT605FLO	
Sets	Heat Duty of stream QTT605XS to 0
Varies	Mass Flow of stream TT605CWS
Purpose	Sets amount of cooling water needed in HEX TT-605-
TT610FLO	
Sets	Heat duty of stream QTT610XS to 0
Varies	Mass Flow of stream TT610CWS
Purpose	Sets amount of cooling water needed in HEX TT-610-

WASTE WATER TREATMENT SECTION

PROCESS DESCRIPTION. The waste water treatment section takes the Beer Tower bottoms and passes then through a centrifuge. This removes 97.375% of the insoluble solids into a 30% concentration. This stream is sent to FUELMIX in the Boiler Section to be used as fuel in the Boiler.

The water stream from the centrifuge is sent to a heat exchanger where the wastewater is cooled to 55°C against cooling water and then sent to the anaerobic digestor (ANAEROB). Also added to the anaerobic digestor is the stream TOWASTE, which is the cooled outlet of heat exchanger TT-615+.

In the anaerobic digestor 84.3% of all soluble organic material, with the exception of lignin, are converted to methane and carbon dioxide. The conversions are given in Table 10, with the figures for COD and then for Methane and Carbon Dioxide

TABLE 11: ANAEROBIC DIGESTER CONVERSION RATES (LB/LB)

COMPONENT	COD	METHANE	CARBON DIOXIDE
Suspended Solids	2.47	0.595	0.398
Xylose	1.07	0.258	0.172
HMF	1.67	0.402	0.269
Furfural	1.67	0.402	0.269
Cellulase	1.7	0.410	0.274
Glycerol	1.22	0.294	0.196
Cell Mass	1.42	0.342	0.229

H2S is also produced, in the anaerobic digestor, as a by-product of the digestion of the soluble and insoluble gypsum. The conversions are given below in Table 12

TABLE 12: ANAEROBIC DIGESTOR HYDROGEN SULFIDE PRODUCTION (LB/LB)

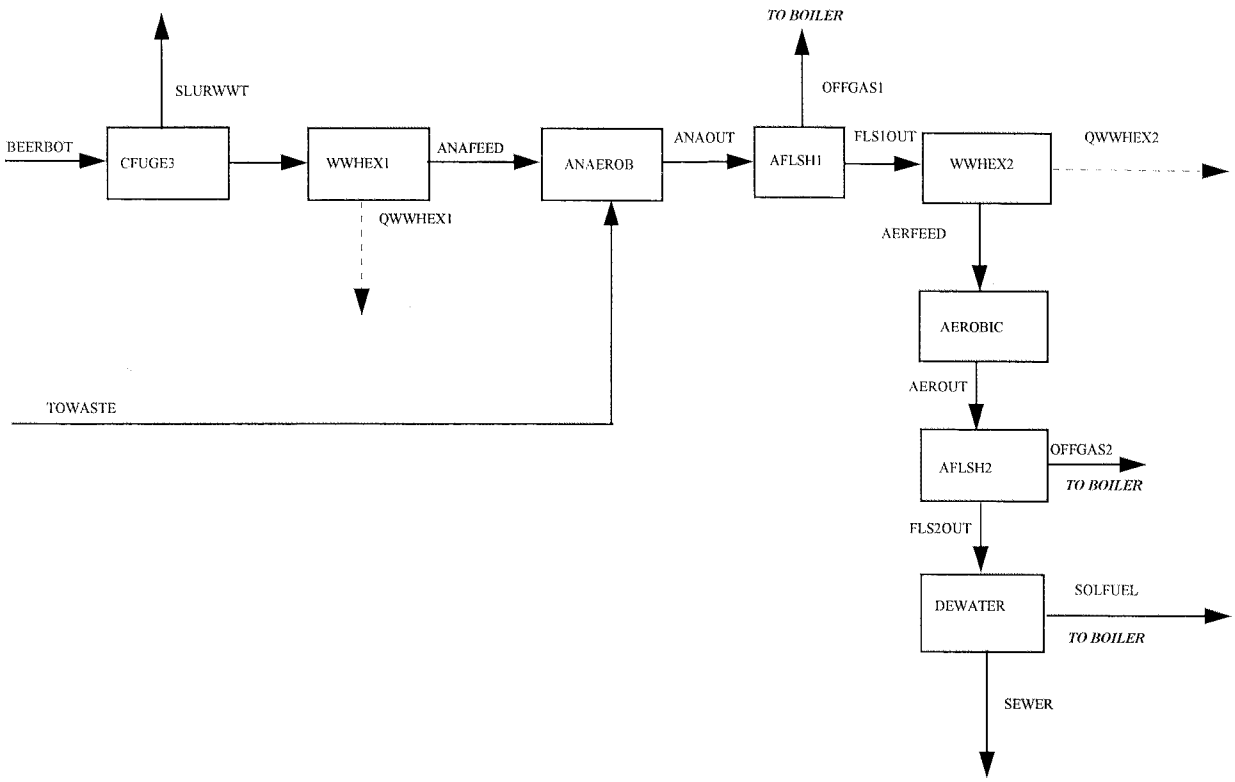
Component	Sulfate	Hydrogen Sulfide
Gypsum (soluble)	0.56	0.141
Gypsum (insoluble)	0.56	0.141

The offgas produced in the anaerobic digestor is sent to the Boiler Section to be used as fuel.

At the outlet of the anaerobic digester, the effluent stream enters a heat exchanger (WWHEX1) where the temperature is lowered to 35°C against cooling water. The stream is then entered into the aerobic digestor, where 97.375 of all the soluble organics, with the exception of lignin, are removed. The effluent from the aerobic digestor is sent to a separator where the lignin and insoluble gypsum are removed to a bottom stream. This stream is 50% water and 50% solids by mass. The remaining water is sent to the sewer.

The solids stream is sent to the boiler Section to be used as fuel.

Wastewater Treatment



BOILER SECTION

The Boiler Section takes all of the designated fuel streams in the flowsheet and converts them into heat and exhaust streams.

PROCESS DESCRIPTION. Slurry feed from the centrifuge product of the Beer Tower bottoms and undigested lignin and other sludge from the Wastewater Treatment Section are mixed together in SLURMIX. The product is fed to the DRYERSEP where the stream is heated so that 50% of the water is removed. The water vapor is sent to the GASCOOL block. The dried slurry is then sent to the Block SLURDRY, where it is heated to 200°F. The SLUROUT stream is then sent to FUELMIX for use as fuel.

Combustion air is raised to 14.9 psi in the COMBFAN and this is sent to the FUELMIX along with streams from the Distillation Section (TT611gas, TT606gas, Toboiler) and the Wastewater Treatment Section (Off-gas). These are combusted in the COMBUSTR unit. The combustion products are sent to HRSG in the stream BOILOUT and the enthalpy of combustion is sent to unit HRSG in stream QCOMBUST. There the combustion products are cooled to 300°F and the enthalpy stream is sent to QCOMSPLT.

To mimic the heat losses in a normal system a 2.75% heat loss is taken in QCOMSPLT. This takes the form of a split stream QCOMLOSS. The remaining heat QBOILER is sent to the BOILER in the Steam Cycle Section.

The combustion gases are sent to a Bag house to remove ash and particulates. The ASH stream is sent off the flowsheet. The fluegas is then sent to a GASCOOL where the stream is cooled to 150°F to provide drying for the SLURDRY unit. The fluegas is then sent off the flow sheet in the stream EXHAUST.

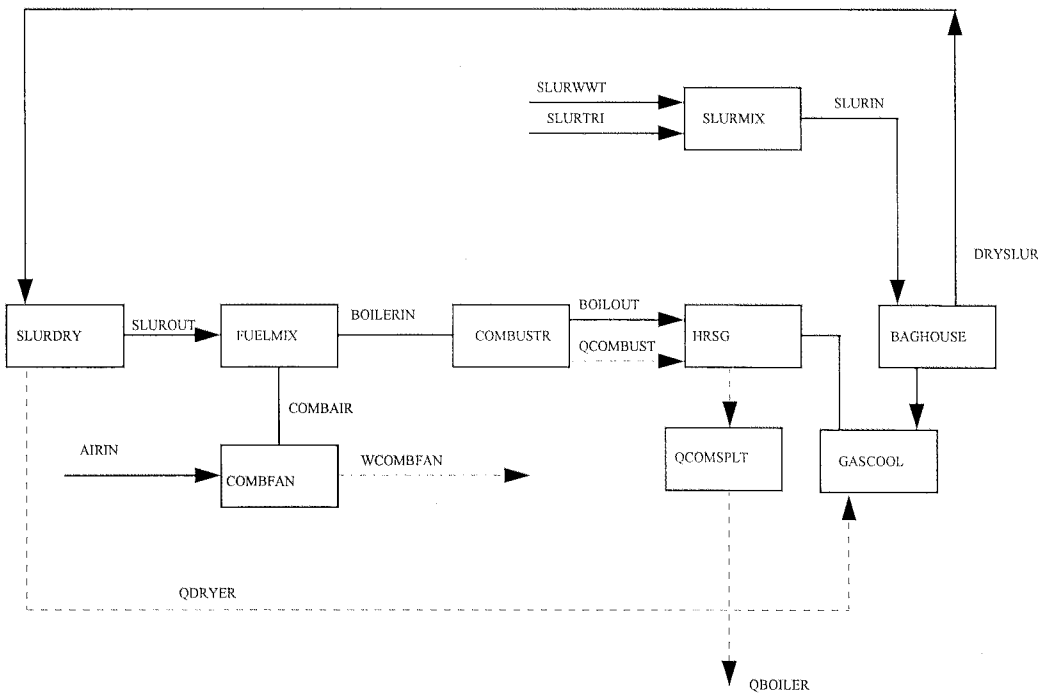
The water which is removed from the slurry is also sent to GASCOOL where it is sent off the flowsheet in stream EXLIQUID.

The combustion reaction used in the COMBUSTR are given in Table 10.

TABLE 13: COMBUSTER REACTION STOICHIOMETRIES AND CONVERSIONS

REACTION	CONVERSION
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	100% CH_4
$C2H4O\text{-}1 + 2.5O_2 \rightarrow 2CO_2 + 6H_2O$	100% C2H4O-1
$FUSELOIL + 7.5O_2 \rightarrow 2CO_2 + 6H_2O$	100% FUSELOIL
$SOLSLDS + 7O_2 \rightarrow 6CO_2 + 3H_2O$	100% SOLSLDS
$ETHANOL + 3O_2 \rightarrow 2CO_2 + 3H_2O$	100% ETHANOL
$GLYCEROL + 3.5O_2 \rightarrow 3CO_2 + 4H_2O$	100% GLYCEROL
$LIGNIN + 7.5O_2 \rightarrow 7CO_2 + 3H_2O$	100% LIGNIN
$ENZYME + 15O_2 \rightarrow 10CO_2 + 8H_2O + NO + 2NO_2$	100% ENZYME
$CELLULAS + 15O_2 \rightarrow 10CO_2 + 8H_2O + NO + 2NO_2$	100% CELLULAS
$CELLULOSE + 6O_2 \rightarrow 6CO_2 + 5H_2O$	100% CELLULOSE
$XYLOSE + 5O_2 \rightarrow 5CO_2 + 5H_2O$	100% XYLOSE
$BIOMASS + 20.5O_2 \rightarrow 15CO_2 + 13.5H_2O + NO + 2NO_2$	100% BIOMASS
$XYLAN + 5O_2 \rightarrow 5CO_2 + 4H_2O$	100% XYLAN

Boiler Section



DESIGN SPECIFICATIONS

CombAir		
	Sets	Mass Flow of stream AIRIN
	Varies	Mass Flow of stream LPSTEAM
	Purpose	Sets air flow to the combuster
SetDryer		
	Sets	H2O Mass flow of stream DRYSLUR to 0.35 times the total Mass Flow of DRYSLUR
	Varies	Fractions of H2O in DRYSLUR
	Purpose	Sets the moisture content of the dyer outlet to 35%

Note: Design Specification for control of Bag House temperature is in the input file, but is not active.

STEAM CYCLE

The steam cycle is a closed loop with the only feed streams being Boiler Feed Water (BFW) and the heat stream from the combuster. Utility steam is produced at two different levels; low pressure saturated steam is at 50 psi; high pressure steam is at 150 psi, saturated condition. Very high pressure superheated steam (1655 psi 950°F) is produced in this Section to drive a series of steam turbines to produce electrical power.

FLOWSHEET COMMENTS. Inside of this flowsheet there are several streams which are split into two different parts with a Design-Specification link. This reduces the number of tear streams in the overall flowsheet and so speeds up the solution time without removing any accuracy.

PROCESS DESCRIPTION. BFW is brought from the utility and pumped to 1715 psi by BFWPUMP. It is then heated to 335°F against 150 psi steam in BFWECON. The hot BFW is then sent to the boiler where 1655 psi saturated steam is produced utilizing the heat produced in the COMBUSTR unit. A 3% blowdown is taken in the Boiler.

The saturated steam is taken to SUPERHTR where the temperature is raised to 950°F against the heat produced in the COMBUSTR unit. The superheated steam is then passed through the HPTURP where the pressure is dropped to 165 psi. This turbine has an isentropic efficiency of 84.5%. The shaft work produced is given in WHPTURB.

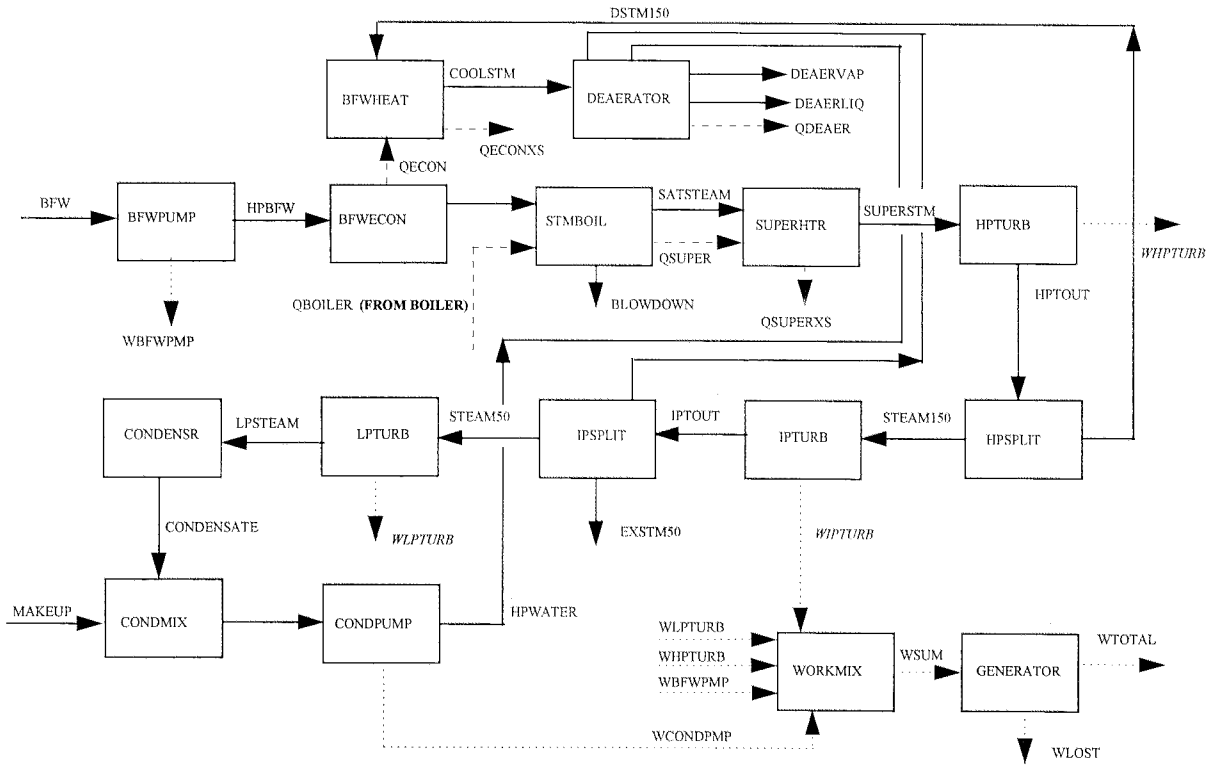
The 165 psi stream is then split into three parts; 5% of the total is sent to the economizer to preheat the BFW; 43000 lb. per hour is sent into the stream EXSTM150; the remainder is sent to the intermediate pressure steam turbine in stream STEAM150.

STEAM150 is fed to IPTURB where the pressure is dropped to 65 psi. The isentropic efficiency of this turbine is also 84.5%. The shaft work produced is in work stream WIPTURB.

The 65 psi steam is then split into three parts; stream DSTM50 is 5% of the total and that is sent to the deareator; stream EXSTM50 is set at 155,000 lb./hr and this is sent off the flowsheet. The remainder of the steam is placed is stream STEAM50 and sent to the low pressure steam turbine.

STEAM50 is fed to LPTURB where the pressure is dropped to 1.72 psi in a condensing turbine. The isentropic efficiency of this turbine is set at 84%. The remaining steam is condensed in the CONDENSR. The makeup water is added in the CONDMIX and the total flow is pumped to the DEAERATR in the HPWATER stream. Also collected in the DEAERATR is the COOLSTM from the BFWHEAT exchanger and the DSTM50 stream. The output of the DEAERATOR is three streams; DEAERLIQ which is equivalent to the BFW stream; DEAERVAP which is the blowdown stream from the deaerator and QDEAER which is the duty stream. Design-Spec DEAERHT sets QDEAR to zero.

STEAM CYCLE



For this section of the flowsheet there are the following Design-Specifications sets:

DESIGN SPECIFICATIONS

DEAERHT	
Sets	Heat duty of stream QDEAR to 0
Varies	Split Fraction of IPSPLIT for Stream DSTM50
Purpose	Controls amount of 50 pound steam to the Deaerator
SETSTEAM	
Sets	Heat Duty of stream QSUPERXS to 0
Varies	Mass Flow of Stream BFW
Purpose	Controls water flow to absorb all duty produced by the combuster
ECONSTM	
Sets	Heat Duty of Stream QECONXS to 0
Varies	Split Fraction of HPSPLIT for Stream DSTM150
Purpose	Controls amount of 150 pound steam to the Economizer

COMPARISON BETWEEN THE ASPEN MODEL AND THE SERI REPORT TP-232-4295

Comparison of the two plants is somewhat difficult as the plant topology has been has changed in the Aspen model from the topology presented in the SERI report. Also there is not a complete material balance reported around many units in the SERI report, so direct comparison is not possible.

PREHYDROLYSIS SECTION

The two input streams, FEED, RCW1 use the same values for mass flows as the ones given in the SERI report. However, in the Aspen case the amount of RCW1 was varied depending upon a design specification for acid concentration in the Prehydrl outlet.

Feed flow was 145140 kg/hr (319,308 lb./hr) in the Aspen case and 320,000 lb./hr in the SERI case.

Recycled water in the SERI case had a flow total of 103,668 lb./hr and then 2878 lb./hrof H2SO4 are added to it to gain a final flow of 106,546 lb./hr. In the Aspen case, the flow of recycled water and acid amounts to 120,330 kg/hr or 264,726 lb./hr. This is a flow more than twice as large as the SERI case and results in larger flows of other components downstream. Combined feed in the Aspen case is 584,034 lb./hr and the SERI case is 426,546 which gives a ratio of 1.37 between the two cases.

Low pressure steam flow in the SERI case is reported at 30,597 lb./hr.

Aspen calculated a flow of 20191 kg/hr or 44420 lb./hr. Ratio (1.45)

High Pressure Steam Flow in the SERI Case is 41354 lb./hr

Aspen Calculated a flow of 28997 kg/hr or 63793 lb./hr. Ratio (1.54)

The Blowdown Flash overhead has a flowrate in the SERI case of 45,797 lb./hr and in the Aspen case 35,183 kg/hr or 77,402 lb./hr. Ratio (1.69). Despite the best attempts of changing the amount of material flashed in this process, the current calculation gives 25% vapor in the Aspen case while the SERI case gives 9%. (We believe that the SERI reported figure is too low for this temperature/pressure configuration.)

The DILBTMS stream corresponds to Stream 218 in the SERI report. Flows of the two streams are 954,844 lb./hr and 942,700 lb/hr, so the basic flow into the overall plant is very close, the main difference being in the split of the recycle water. The Aspen case has more recycled water entering the prehydrolysis reactor and the SERI case has the recycled ware entering the blowdown tank.

OVERLIMING

Lime flowrate in the Aspen case is 1966.5 kg/hr (4325.2 lb/hr) which is roughly twice the amount required by the SERI case. However the lime is sued to control the pH of the stream and not just for neutralization as in the SERI case.

SOLIDS SEPARATION

This section is not in the plant topology of the SERI report so no comparisons can be made. Stream 223 in the SERI case is the feed to the Xylose Fermentation. Its composition and flowrate are compared to Cooliq in the following chart.

TABLE 14: COMPARISON OF XYLOSE FERMENTATION FEED STREAMS

COMPONENT	STREAM 223	COOLIQ
Water	751012	705110.7
Cellulose	70200	2832
Xylan	2636	80
Soluble Solids	15157	10134
Ash	541	20
Lignin	38012	1532
H2SO4	0	0
Glucose	2410	2037
Xylose	37276	23379
HMF	98	29.4
Furfural	0	112
Lime	0	0
Gypsum	5667	198
Glycerol	1358	705
Biomass	335	8.83
Galactos	N/A	58
Mannose	N/A	199
Arabinos	N/A	78
Arabinan	N/A	6
Mannan	N/A	38

The flow rate of water and the soluble solids are fairly close, however the insoluble solids have been removed and sent further downstream to the SSF section.

Comparisons of compositions and flowrates in the Xylose, Cellulase and SSF sections are almost impossible, because of the changes in the topology. A comparison of the flows exiting the SSF Fermenter, where most of flows have been recombined is shown below.

TABLE 15: COMPARISON OF SSF SECTION OUTLET

COMPONENT	STREAM 510	STREAM 507	SSFLIQ	VENT	TOTALS
Water	832,639	655	765169	1596	766765
Cellulose	8861		8805	0	8805
Xylan	539		397	0	397
Soluble Solids	16263		10246	0	10246
Ash	581		521	0	521
Lignin	38892		38136	0	38136
H2SO4	0		0	0	0
Glucose	0		8089	0	8089
Xylose	7638		7569	0	7569
HMF	105		43.5	45.21	88
Furfural			128	133	261
Lime			8	55	63
Gypsum	5886		10397	0	10397
Glycerol	911		0	2562	2562
Biomass			2827	0	2827
Galactos			147	0	147
Mannose			497	0	497
Arabinos			1579	0	1579
Arabinan			29.97	0	30
Mannan			48.95	0	49
Cellulase	657		222	0	222
Ethanol	39007	4237	14606	22682	37288
Fuseloil	76		0	33	33
Acetaldehyde	6940		2.72	972	975
CO2		27457	94	36206	36300
O2				1175	1175
NH3				3	3
N2				4353	4353

As is clear in this table the totals of many components in the two streams are very close,

- Ethanol
- Xylose
- Cellulose
- Lignin
- Ash

the component makeup of the streams are very different. In the Aspen case a great deal of the ethanol is sent overhead, while in the SERI case no ethanol is in the vapor stream.

The SERI report does not include any of the air associated with the reactor, residual sugars, residual starchesor non-reacted components, so there are no values for

- Galactos
- Mannose
- Arabinan
- Mannan
- NH3
- N2
- O2
- Lime
- Biomass

There are discrepancies in the water flow rate and in the amounts of acetaldehyde, glycerol, Soluble solids and gypsum.

The discrepancy for water can partially be explained in the stream which is split off at the beginning of the Xylose fermentation section as a batch stream. This stream has a flow rate of 3500 lb/hr of water and small amounts of ethanol, cellulose, and lignin. Additional amounts of water, and ethanol are lost in the flash streams which are present at the exit of each reactor, SSFFLVAP, CLFL1OV, CLFL2OV, and XYLSFLOV. An additional 5 moles of water would be created for each of the remaining moles of glucose when that was converted into biomass.

The discrepancy between glycerol and acetaldehyde can be traced back to the formation of these components in the SSF Fermentation reactor. They are formed in almost equal amounts 22.14 moles of each. The difference in lb/hr is due to the much higher molecular weight of glycerol, 96.085 lb/mole versus 44.054 lb/mole and due to the fact that there are roughly 5 moles per hour of glycerol arriving at the SSF reactor from stream SSFFD1.

The flow rate of gypsum differs from the SERI because of two factors. First, the difference in the split between the recycle water streams results in a higher amount of acid flow into the overlime reactor. Second, the use of lime to raise the pH of the stream to 10 and the resulting neutralization of the stream with acid in the NEUTRALIZER results in a higher amount of gypsum in the Aspen system than in the SERI system.

The flow rate difference of soluble solids is due to a discrepancy in the concentration of the soluble solids in the second recycle water stream. This has been corrected and will disappear in future runs of the flow sheet.

After the exit of the SSF reactor section, the streams composition changes only due to the difference in split factors and recoveries in the distillation section. There should be no large discrepancies in the performance of the Aspen model and the SERI report except for those due to the topologies in the plant layout.

APPENDIX A: RATIONAL FOR SELECTION OF PHYSICAL PROPERTY CONSTANTS

The Aspen program requires a minimum set of physical properties in order to function properly. For non-library components these are:

- Molecular Weight
- Critical Pressure
- Critical Temperature
- Pitzer's Omega
- Antoine Vapor Pressure Constants
- Gibbs Free Energy of Formation
- Heat of Formation

The sources of known data used in the Aspen model are as follows:

- Heats of Formation were supplied by NREL.
- Free energy of formation were supplied by NREL.
- Molecular Weights were either calculated from chemical formulas or were supplied by NREL

The critical Temperature, Critical Pressure and Omega were estimated in the following manner.

Using the book "The Properties of Gases and Liquids," critical Values for very high molecular weight compounds were analyzed. This provided initial estimations, most values for hydrocarbons are roughly 750K for Tc , 15 atm for Pc and 0.75 for Omega. After this initial guess the values were altered to manipulate the K values in the Blowdown Flash Unit operation. Keeping the Omega and Tc constant as the critical Pressure was lowered, the K values were reduced to a point where the components were no longer volatile. These values were then used for the remainder of the components. For components which had no volatility under any circumstances, the Pc was lowered even more.

The first Antoine constant for all components was set to -1.0E8. All other constants were set to zero. This makes the component have an extremely low vapor at all temperatures.

COMPONENT DATABANK

Component	MW	Pc	Tc	Dgsfrm	Dhsfrm	Omega
H2O	18.0152					
Ethanol	46.0688					
Fuseloil	88.1492					
N2	28.0134					
CO2	44.0098					
O2	31.9988					
H2SO4	98.0734					0.40
CaSO4	136.1376	250	1000	-142000		0.215
Cellulos	162.142	150	700	-217152	-230769	0.96
Xylan	132.1158	150	700	-175824	-183469	0.96
Arabinan	132.1158	150	700	-175824	-183469	0.96
Mannan	162.142	150	700	-217152	-230769	0.90
Galactan	162.142	150	700	-217152	-230769	0.90
Solslds	162.142	150	700	-217152	-230769	0.75
Glucose	180.1572	150	700	-217152	-303392	0.75
Xylose	150.131	150	700	-175824	-253225	0.75
Galactose	180.1572	150	700	-219541	-303392	0.75
Mannose	180.1572	150	700	-175824	-253225	0.75
Arabinose	150.131	150	700	-217152	-253225	0.75
Biomass	246.2626	150	700	-355000	-323000	0.90
Lignin	122.1232	100	800	-379838	-217152	0.96
Gypsum	172.168	100	800	-201000		0.215
HMF	126.1116					
Cellulas	226.2547	150	800			0.96
CaH2O2		100	750	-230769		0.215

APPENDIX B: PH CALCULATION

In the OVERLIME unit, Calcium Hydroxide (CA(OH)2 or Lime) is added to neutralize any remaining sulfuric acid (H2SO4) and to raise the Ph of the stream to 10. The calculations are done as follows:

MH2O = The mass flow of Water

VH2O = The volumetric flow of Water in liters

*M*Ca(OH)2 = Molar Flow of Calcium Hydroxide

ConcCa(OH)2 = Molar Concentration of Ca(OH) = *M*Ca(OH)2 / VH2O

pOH = -log[2* ConcCa(OH)2]

pH = 14 - pOH

APPENDIX C: REACTOR DESIGN SPECIFICATIONS

There are two types of design specifications for the reactors. The first involves specifying the amount of air required for the reactor; the second specifies the amount of ammonia to be supplied to the reactor. The Air Requirement specification is shown below:

```
Design-Spec AirX
  Define FliqX Stream-Var Stream=Reactor Outlet Stream Var=Mass-Flow
  Define FairX Stream-Var Stream=AirfdX Var=Mass-Flow
  Define DairX Stream-Var Stream=AirfdX Var=Mass-Density
  Define DliqX Stream-Var Stream=Reactor Outlet Stream Var=Mass-Density
F   VfactX=0.95
F   RtimeX= 1
F   afactX=10.
F   vollqX=FliqX/0.796 is assumed density of liquid phase
F   volrqX = (vollqX *  RtimeX * 24 * 60 * afactX)/ vfactX
F   volarX = FairX/DairX
F   reqX = volrqX-volarX
  Spec 'reqX' To '0'
  Tol-Spec 0.1
  Vary Stream-Var Stream=AirfdX Var=Mass-Flow
  Limits Lower=0 Upper=200
```

This specification calculates the air requirement by using the volume of the liquid, plus some factors for residence time and multipliers for volume of air to volumes of liquid. **This specification does not address the actual oxygen demand in the reactor, therefore it is possible to have the reactor go into an oxygen deficit condition. This will be reported in the *.his (History) file. When an oxygen deficit condition occurs, conversion factors are reset inside the reactor. When the conversion factors are reset they are left in that condition for the remainder of the simulation.**

The design specifications for the ammonia flowrates are shown below:

```
Design-Spec AmmoX
  Define AmmonX Mole-Flow Stream=Reactor Outlet Stream  Component=NH3
  Spec 'AmmonX' to '0.2'
  Tol-Spec 0.05
  Vary Stream-Var Stream=NutrX Var=Mass-Flow
  Limits Lower=0 Upper=250
```

This sets the flow of ammonia into the reactor to such a level that the demand for ammonia is supplied and there will be an excess of 0.2 moles in the outlet stream. If the number in the outlet stream is reduced to 0 there are some convergence problems which occur. The excess ammonia can be removed in an extra splitter to an extra stream if this interferes with the simulation.

---

*The method used to converge the design specifications is to take the starting value from the flow-rate of the stream itself and divide the difference between the limits into 10 increments and use these for the step size. It is imperative that the starting value for the air stream be above the required value for the oxygen demand otherwise the conversion values will be reset by Aspen.